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FRICTION BEHAVIOR OF MEMBERS OF THE PLATINUM METALS GROUP WITH GOLD

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FRICITION BEHAVIOR OF MEMBERS OF THE PLATINUM METALS GROUP WITH GOLD

by Donald H. Buckley

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SUMMARY

An investigation was conducted to determine the adhesion and friction behavior of metals of the platinum group. Experiments were conducted with a gold single crystal of the (111) orientation contacting and sliding single crystal surfaces of the platinum metals of the (111) or (0001) orientation. The surfaces were examined clean and in the presence of oxygen, vinyl chloride (C_2H_3Cl), or methyl mercaptan (CH_3SH). Adhesion and sliding experiments were conducted at loads of from 1 to 10 grams. Sliding was at a speed of 0.7 millimeter per minute. Low energy electron diffraction (LEED) and Auger spectroscopic analyses were used to monitor surface cleanliness and the presence of various adsorbed species.

The results of the investigation indicate that differences in friction properties exist with the various platinum metals contacting gold. These differences are believed to be due to a difference in the chemical bonding of these metals. Adsorption of the species oxygen, vinyl chloride, and methyl mercaptan was selective. These substances adsorbed readily on some of the platinum metals reducing friction while on other surfaces they did not adsorb at all. Even when these materials did adsorb in some instances they did not eliminate adhesion - for example, vinyl chloride on a palladium surface.

INTRODUCTION

The metals of the platinum metals family of elements and their alloys have been used extensively in electrical contacts - both the make and break type and sliding or rubbing contacts (ref 1). The elements involved are ruthenium, rhodium, palladium, osmium, iridium, and platinum. Their atomic numbers are, respectively, 44, 45, 46, 76, 77, and 78.

The platinum metals, in general, are not very reactive with environmental constituents and lubricants. They are good catalysts and have been found in electrical contact

studies to initiate polymerization of environmental organic vapors (ref. 2). The adhesion, friction, and lubricated behavior of these metals as a group has not been explored. Such a study could facilitate the proper selection of these metals in contact applications.

In practical electrical contact systems these metals are generally not used in contact with themselves but rather in contact with some other metal or alloy. Many of these systems used in the aerospace industry must operate in a vacuum. Frequently the contacting mating surface will be either copper or one of the other noble metals, gold or silver.

The objective of the present investigation was to examine the adhesion and friction properties of the platinum metals both clean and lubricated with oxygen, vinyl chloride, and methyl mercaptan. All members of the group were examined except osmium, which is extremely brittle and difficult to obtain in the specimen size required herein. The group members were all in single crystalline form. The highest atomic density, lowest surface energy planes were studied. For the face-centered-cubic metals it was the (111) plane and for ruthenium having a close packed hexagonal structure it was the (0001) or basal plane. The mating metal surface was a single crystal of gold with the (111) plane parallel to the sliding interface. Both low energy electron diffraction (LEED) and Auger spectroscopic analyses were used in the identification and characterization of the surfaces of the platinum metals.

MATERIALS

All of the platinum metals were 99.99 percent pure or better, and the gold for the pin specimen was 99.999 percent pure. Some properties of these metals are presented in table I. These properties shall be discussed later in reference to the experimental adhesion and friction data obtained in this investigation.

APPARATUS

The apparatus used in this investigation was a vacuum system having built into it the capabilities for measuring adhesion, load, and friction. The apparatus also contained the surface analytical tools, Auger and LEED analyses. The mechanism for measuring adhesion, loading, and friction is shown schematically in figure 1.

A gimbal mounted beam projects into the vacuum system. The beam contains two flats machined normal to each other with strain gages mounted thereon. The end of the rod contains the gold single crystal pin specimen. As the beam is moved inward toward the disk a load is applied which is measured by the strain gage. If adhesion occurs when the load is removed, the adhesion forces are measured by the deflection of the beam in the direction opposite to which the load was applied (see fig. 1).

Tangential motion of the pin along the disk surface is accomplished through the gimbal assembly. Under an applied load friction force is sensed by the strain gage normal to that used to measure load.

Almost any sensitivity desired can be achieved by proper thinning of the flats in the beam. In the present study full scale deflection on a conventional strip chart recorder resulted from a 10 gram load, adhesion, or friction force.

Multiple wear tracks could be generated on the disk specimen surface by translational motion of the beam containing the pin. Pin sliding was in the vertical direction as shown in figure 1.

The vacuum apparatus in which the components of figure 1 were contained also had a LEED system and an Auger spectrometer. The electron beam of both could be focused on any disk site desired.

The data of figure 2 were for gold sliding on clean platinum. The Auger spectroscopic analysis of the platinum surface after sliding indicated the transfer of gold to the platinum surface with single pass sliding. Thus, the friction data (clean) of figure 2 are a reflection of the shear behavior of gold. The adhesive interfacial bond strength was stronger than the cohesive gold bond strength. Such results are consistent with the properties presented for these two metals in table I and normally associated with tangential shear behavior.

In order to determine surface film effects on friction, the clean platinum was exposed to oxygen at a pressure of 6.65×10^3 newtons per square meter (50 torr) after the ion pump was turned off for a period of 30 minutes. The system was then evacuated to 1.33×10^{-8} newton per square meter (10^{-10} torr), an Auger spectroscopic analysis was made to confirm the presence of oxygen on the platinum surface, and a friction experiment was conducted at various loads. The Auger trace showing the oxygen peak therein is presented in figure 3. The friction results obtained are presented in figure 2.

Figure 2 indicates a marked decrease in the friction force with load for platinum (111) covered with oxygen. Furthermore, beyond a 4-gram load no change in friction force was observed with further load increases to 10 grams. The amount of oxygen on the surface at saturation is a monolayer or less.

A LEED analysis of the surface revealed a diffuse pattern. A $(2 \times 2) - 0$ surface structure as defined in reference 3 has been observed for oxygen on platinum (ref. 4).

Palladium

Friction experiments similar to those conducted with platinum were conducted with a palladium (111) surface (fig. 4). The palladium surface was first cleaned by argon sputter bombardment. An Auger spectrum for the clean palladium surface is presented in figure 5(a). The upper friction curve was obtained at various loads. It should be

indicated that the ordinate in figure 4 is different from that in figure 2. The friction force for gold on palladium was less than for gold on platinum (111) surface at all loads.

With oxygen present on the palladium surface the friction was markedly less than was observed for the clean metals in contact. Unlike with the platinum, the friction force in the presence of surface oxygen decreased with increasing load. Despite this decrease and the generally lower friction than was obtained with the clean surface, gold transferred to the palladium both in the presence and absence of oxygen. The presence of the gold and oxygen on the palladium surface is shown in the Auger spectrum of figure 5(b).

The basic LEED pattern for the palladium (111) surface was not altered by the presence of oxygen. The diffraction spots became more diffuse. Oxygen has been observed on the (110) surface of palladium in ordered structures but not on the (100) and (111) orientations (ref. 3).

The interaction of organic molecules with metals such as palladium is of interest in electrical contacts where polymer films have been observed to form in the presence of such materials. A clean palladium (111) surface was exposed to vinyl chloride (C_2H_3Cl) monomer at a pressure of 6.65×10^3 newtons per square meter (50 torr) for 30 minutes. The system was then evacuated to 1.33×10^{-8} newton per square meter (10^{-10} torr) and the surface analyzed with an Auger analysis. The spectrum obtained is presented in figure 5(c). In addition to the palladium peaks a chlorine peak was observed. The carbon Auger peak would normally appear between the first two palladium peaks of figure 5(c). The carbon Auger peak occurs at 272 electron volts and the center palladium peak at 279 electron volts. It would appear from the spectrum that dissociative adsorption of the vinyl chloride occurs with only chlorine remaining on the surface.

Even with chlorine present on the palladium surface strong adhesion of the gold to the palladium was observed. Adhesion forces measured at various loads in the presence of the surface film are presented in figure 6. The adhesion force is linearly proportional to applied load. These results indicate that strong adhesion can occur to metals even in the presence of adsorbed surface films.

Rhodium

The friction behavior of clean rhodium is discussed with the presentation of the ruthenium data since the friction behavior of gold in contact with these two metals was nearly the same. Friction data were also obtained for various materials adsorbed to the rhodium (111) surface. The materials included oxygen, vinyl chloride, and methyl mercaptan (CH_3SH).

The rhodium (111) surface was exposed to each of the aforementioned adsorbates for a period of 30 minutes at a pressure of 10 micrometers. Thus, the exposure of the clean rhodium surface was the same for each of these species. The pressures employed and the exposure times are sufficient to permit the saturation of the surface with each of the species. The data obtained in these experiments are presented in figure 7.

An examination of figure 7 indicates that the friction force increases linearly with load increases in accord with Amonton's Law but that the slope changes with load increases beyond 5 grams for rhodium with all three adsorbates present on the rhodium surface. With methyl mercaptan (the sulfur containing adsorbate) the friction force did not increase markedly with increased loading to 5 grams. Beyond 5 grams the friction force began a rapid increase with further increases in the applied load. In general, however, the sulfur was more effective in reducing friction for rhodium than was either oxygen or chlorine. All three species were adsorbed on the rhodium surface. The presence of chlorine from vinyl chloride on the rhodium surface can be seen in the Auger spectrum of figure 8.

The observation that sulfur is more effective than oxygen in minimizing friction is consistent with earlier observations for iron. With equivalent surface coverages of oxygen and sulfur on an iron (110) surface friction was unaffected by increases in load with the sulfide film while friction increased continuously with oxygen and increased loading (ref. 4). The present study indicates that rhodium like iron is afforded greater surface protection with sulfur than it is with oxygen.

Ruthenium

Friction measurements were made with a gold (111) surface sliding on clean ruthenium and rhodium. The results obtained are presented in figure 9. Two observations can be made relative to the data of figure 9: The first is that there is a linear relation between friction force and load, and the second is that both ruthenium and rhodium exhibit essentially the same friction behavior when contacted by gold.

This second observation is important in that it shows that the friction force for these two metals in contact is essentially dictated by the properties of gold. Earlier studies with ruthenium sliding on ruthenium and rhodium sliding on rhodium in the clean state indicate marked differences in their friction behavior (ref. 5). Friction coefficients of 0.6 and 3.75 were reported in reference 5 for ruthenium and rhodium, respectively. The marked difference in friction behavior between these two metals was predictable prior to measurement from crystal structure considerations.

In the present study Auger spectroscopy revealed that gold transferred to both the ruthenium and the rhodium. Table I presents the basic properties of the three metals which might be expected to influence adhesion and, accordingly, friction behavior. Ru-

ruthenium and rhodium have higher cohesive energies, heats of sublimation, shear strengths, and hardness. As was previously observed with platinum and palladium, gold adhered to the ruthenium and rhodium surfaces. The interfacial adhesive bond between gold and these metals was stronger than the cohesive bond in gold which was responsible for the friction behavior seen in figure 9.

It is worth noting at this point that in all contacts between dissimilar metals when the surfaces are clean the cohesively weaker metal transfers to the cohesively stronger metal. This implies that the adhesive junctions and the corresponding bonds are stronger than the cohesive bonds in the weaker of the two metals.

Ruthenium had a relatively inert surface chemically. Exposure of ruthenium to vinyl chloride and methyl mercaptan failed to yield, as determined by Auger spectroscopy, any uptake of these substances. Even with oxygen little or no adsorption occurred as indicated by the Auger spectrum of figure 10. Furthermore, the friction behavior remained relatively unchanged after exposing the ruthenium to 50 micrometers of oxygen for 30 minutes. The basal (0001) orientation of ruthenium was examined in these studies. It is the least chemically active. Other more active planes may adsorb some of the species.

Iridium

The friction force for iridium at various loads when contacted by gold was measured and the results obtained are presented in figure 11. An examination of figure 11 indicates that the friction force increases linearly with load. The friction force is, however, extremely low. This is discussed later.

The friction data of figure 11 are for a single pass of the gold (111) pin across the disk surface after the surface was clean. Prior to cleaning the surface contained carbon and oxygen in sufficient quantity (excess of four atomic layers) such that the iridium Auger peaks could not be detected as indicated in figure 12(a). After argon ion sputter bombardment the Auger spectrum of figure 12(b) was obtained and it revealed all of the iridium peaks with an absence of carbon and oxygen.

The extremely low friction force for single pass experiments in figure 11 prompted additional experimentation where repeated passes were over the same surface. The results obtained in such experiments are presented in figure 13. With increasing passes of the gold (111) pin across the same track on the iridium (111) surface the friction continuously increased to six passes. From six to ten passes no further change in friction force was observed.

The results of figure 13 together with Auger results indicate increasing uptake of gold on the iridium surface with repeated passes to six. The observations indicate an increasing transfer of gold to the iridium surface.

The friction of the other platinum metals continued to increase with increasing load beyond 6 grams. Iridium has a relatively poor chemical affinity for gold while for platinum and palladium the chemical affinity for gold is relatively strong (ref. 7). A weaker adhesive interfacial bonding of gold to iridium may therefore account for the results of figure 13.

Attempts were made to adsorb oxygen, vinyl chloride, and methyl mercaptan to iridium but these gases would not adsorb. The iridium was exposed to a pressure of 50 micrometers for each of these gases.

Clean Platinum Metals

Figure 14 is a summary figure of the friction data obtained for a gold (111) surface in sliding contact with the various platinum metals except osmium. The figure indicates that even though the pin was identical for all platinum metals and the transfer of gold occurred to all of the platinum metal surfaces differences in friction behavior existed.

The highest friction was obtained with the metals platinum and palladium and the lowest with ruthenium, rhodium, and iridium. All metals were in single crystal form with the highest atomic density, lowest surface energy plane exposed to contact with gold. These atomic planes have the same atomic packing. These orientations were selected to eliminate crystallographic orientation as a variable.

Both platinum and palladium are chemically more active than ruthenium, rhodium, and iridium. This fact was demonstrated in the present study in that while surface species such as oxygen bonded more readily to metals such as platinum and palladium they showed very weak or no bonding to the other metals. The adsorption characteristics and friction behavior of the platinum metals with various surface conditions are presented in table II.

As the atomic number in period 5 containing the elements ruthenium, rhodium, and palladium is increased, the contribution to bonding of d electrons is increased. Likewise, a similar behavior is observed in period 6 with the elements osmium, iridium, and platinum (ref. 6). Thus, stronger bonding of gold to platinum and palladium would be anticipated from the valence-bond model when that model is applied to metallic systems. As indicated in reference 6 there is no reason not to apply it to metal systems since it involves the same basic electronic bonding as is involved in other systems for which the model was originally developed.

In considering the transition elements a knowledge of the contribution of d electrons to metallic bonding is necessary. An examination of the heats of atomization of the elements in the periodic table clearly indicates the importance of the d electrons to bonding. The most stable metallic structures are those which use as many d electrons as possible in bonding. The contribution to d electron bonding increases with

increasing atomic number; thus, Ru < Rh < Pd and Os < Ir < Pt (see table III). With increasing d electron bonding there is a corresponding decrease in the sp electron contribution to bonding.

CONCLUSIONS

Based on the experimental results obtained in this investigation, when a gold single crystal (111) surface slides on single crystals of members of the platinum metals group the following conclusions are drawn:

1. Gold transfers to all the platinum metals in sliding. Despite this observation the friction force recorded for gold contacting the various platinum metals is different. The metals exhibiting the highest friction are the most active chemically and contribute the greatest amount of d valence electron bonding.
2. Oxygen adsorbed to platinum and palladium quite readily and inhibited adhesion and reduced the friction force observed with the clean metals.
3. Oxygen, vinyl chloride, and methyl mercaptan did not adsorb to the ruthenium (0001) surface and therefore did not inhibit the adhesion or reduce the friction force for ruthenium.
4. Strong adhesion forces were observed for gold-palladium contacts in the presence of vinyl chloride films.
5. Sulfur afforded rhodium greater surface protection than did either vinyl chloride or oxygen where the surface was saturated with films of each of these species.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 8, 1975,
506-16.

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TABLE I - SOME PROPERTIES OF MEMBERS OF THE
PLATINUM METALS FAMILY AND GOLD

Metal	Cohesive energy		Heat of sublimation		Valancies
	J/g atom	kcal/g atom	J/mole	kcal/mole	
Platinum	5.43×10^5	134.8	5.73×10^5	137	2, 4
Palladium	3.75	89.9	4.60	110	2, 4
Iridium	6.65	158.9	5.02	120	3, 4
Rhodium	5.56	133.0	4.80	115	3, 4
Ruthenium	6.43	154.0	5.02	120	6, 4, 8
Osmium	7.82	187.2	-----	---	-----
Gold	3.66	87.6	3.85	92	1, 3

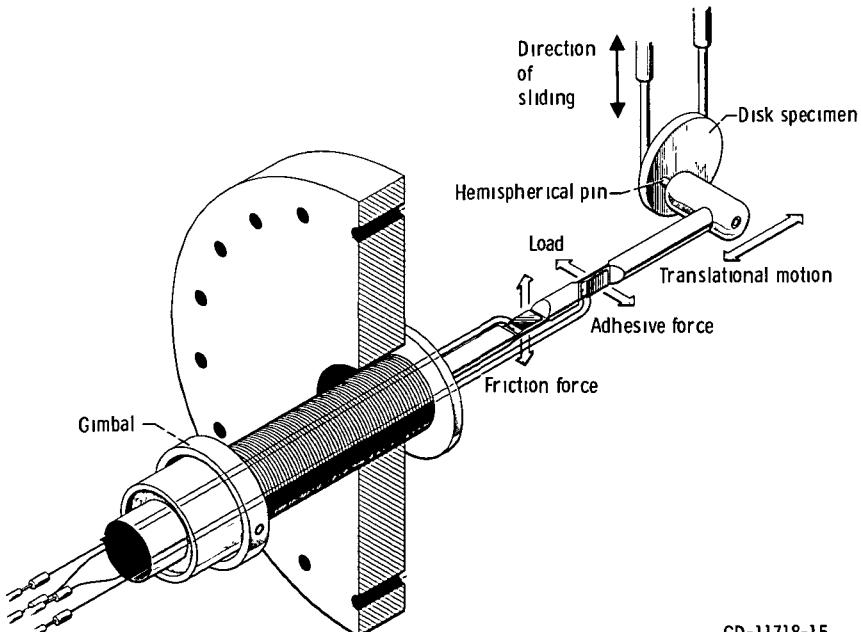
TABLE II - FRICTION COEFFICIENTS
OF PLATINUM METALS

Metal	Metal surface condition			
	Clean	Oxygen	Vinyl chloride	Methyl mercaptan
	Friction coefficient			
Ruthenium (0001)	1.0	^a 1.0	^a 1.0	^a 1.0
Rhodium (111)	1.0	1.0	1.0	8
Palladium (111)	2.2	18	16	15
Iridium (111)	^a 4	4	^a 4	^a 4
Platinum (111)	4.0	1.0	8	7

^aDid not adsorb

TABLE III. - PERIODIC TABLE OF THE ELEMENTS

1 H															2 He		
3 Li	4 Be																
11 Na	12 Mg																
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw				



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Figure 1. - High-vacuum friction and wear apparatus

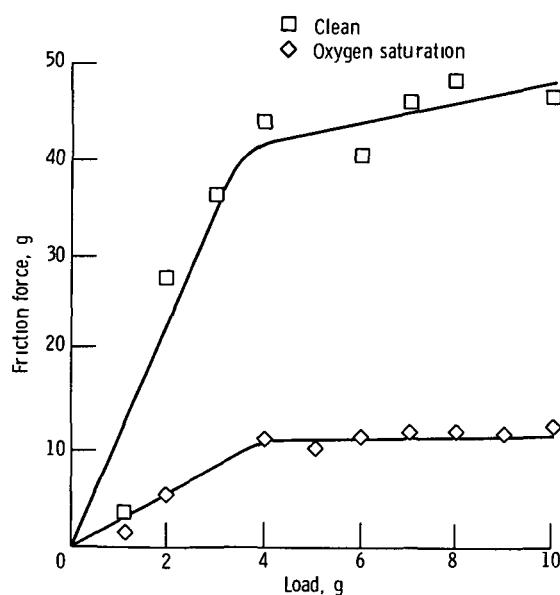


Figure 2 - Friction force as function of load for gold (111) single crystal sliding on platinum (111) single crystal. Sliding velocity, 0.7 millimeter per minute, ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr), and temperature, 23° C

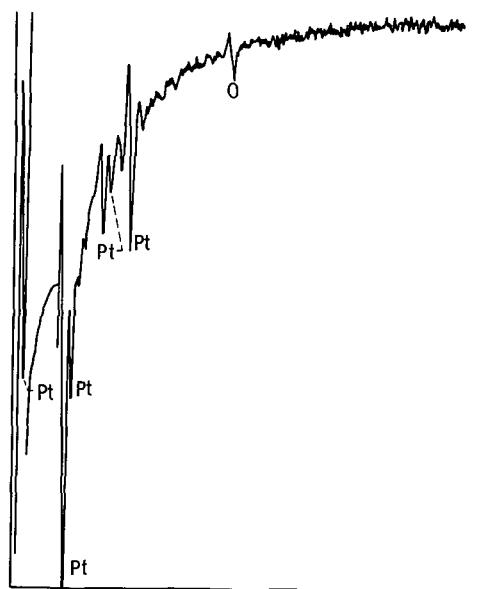


Figure 3 - Auger spectrometer trace of platinum (111) surface after exposure to oxygen. Total oxygen exposure, 6.65×10^3 newtons per square meter (50 torr) for 30 minutes, spectrum obtained at 23° C and 1.33×10^{-8} newton per square meter (10^{-10} torr)

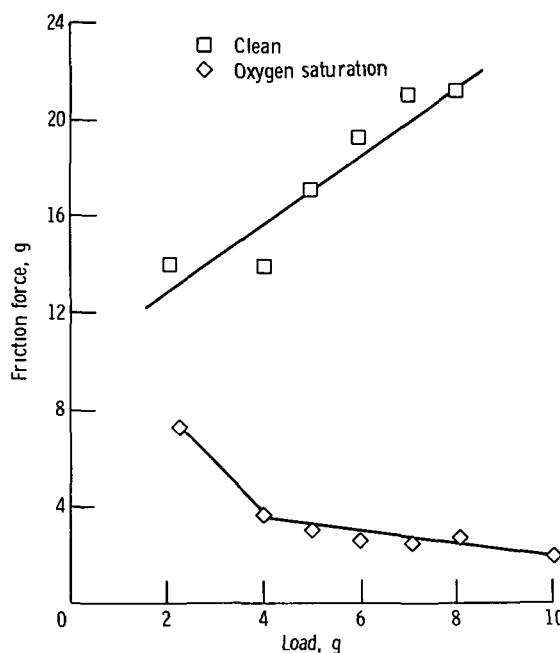
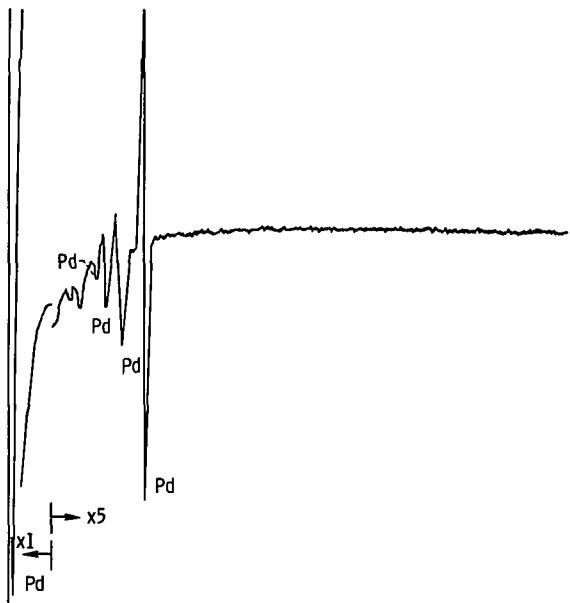
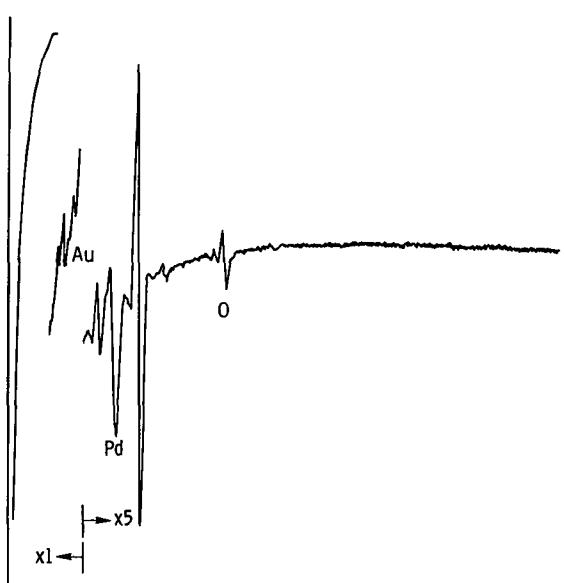


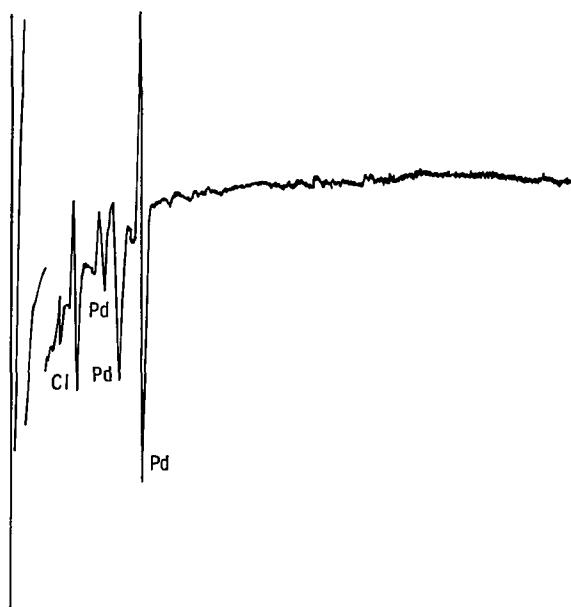
Figure 4 - Friction force as function of load for gold (111) single crystal sliding on palladium (111) single crystal. Sliding velocity, 0.7 millimeter per minute, ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr), and temperature, 23° C



(a) After sputter cleaning and heating Argon sputter, 1.33×10^3 newtons per square meter (10 torr) and 1000 volts for 30 minutes, heated to 500°C for 2 minutes



(b) Saturated with oxygen after sliding gold (111) surface on palladium (111) surface.



(c) After exposure to vinyl chloride Exposure for 30 minutes at pressure of 6.65×10^3 newtons per square meter (50 torr).

Figure 5 - Auger spectrum for palladium (111) surface

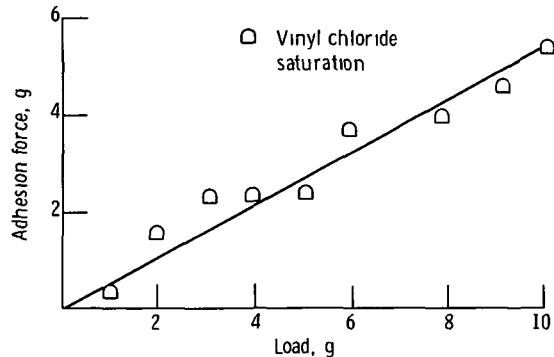


Figure 6 - Adhesion force as function of load for gold (111) single crystal in contact with palladium (111) single crystal. Sliding velocity, 0.7 millimeter per minute; ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr), and temperature, 23°C

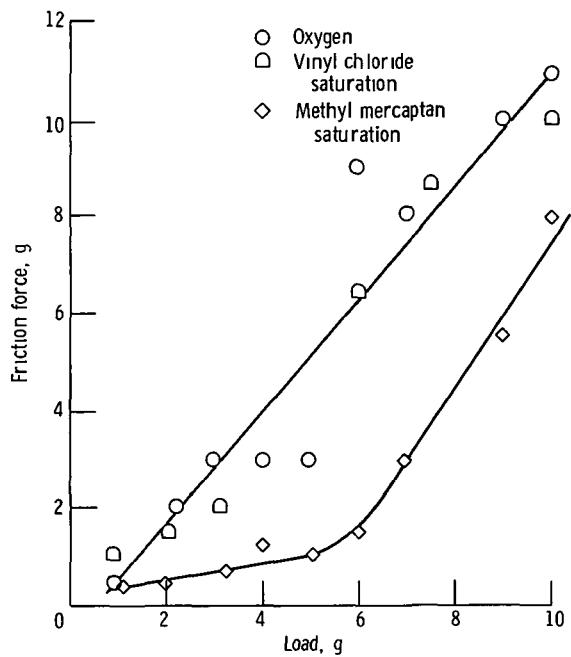


Figure 7 - Friction force as function of load for gold (111) single crystal sliding on rhodium (111) single crystal. Sliding velocity, 0.7 millimeter per meter, ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr), temperature, 23°C

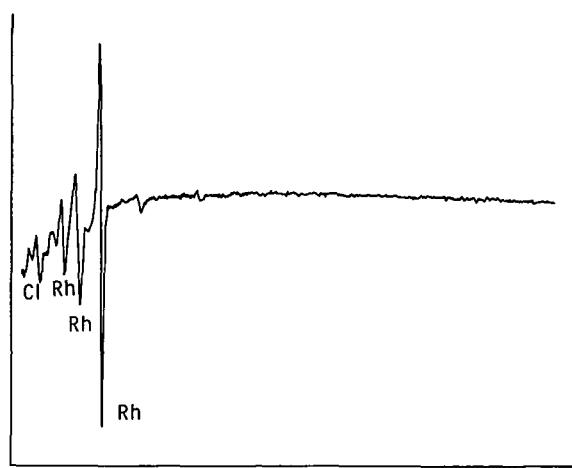


Figure 8 - Auger spectrum for rhodium (111) surface exposed to vinyl chloride. Exposure of 50 micrometers for 30 minutes

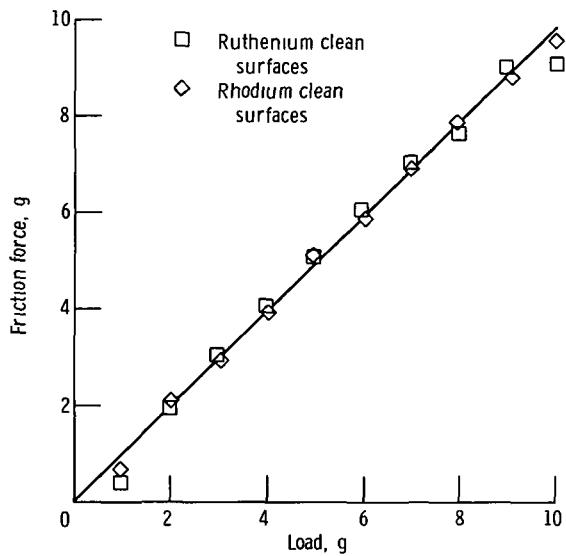


Figure 9 - Friction force as function of load for gold (111) single crystal sliding on ruthenium (0001) and rhodium (111) single crystals. Sliding velocity, 0.7 millimeter per meter; ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr), and temperature, 23°C .

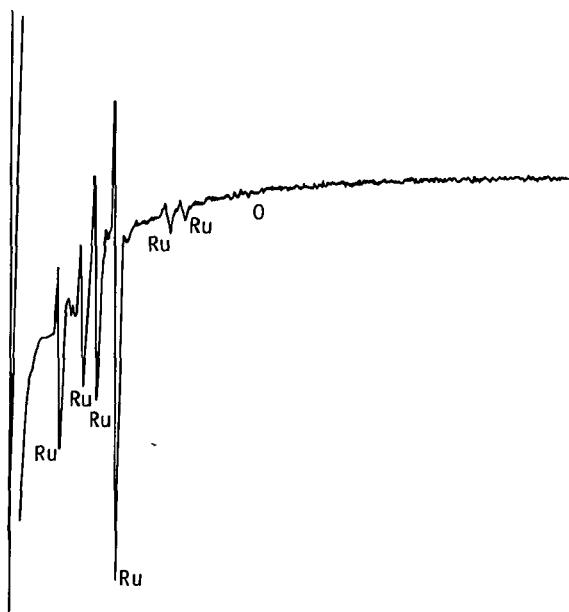


Figure 10. - Auger spectrum for ruthenium (0001) surface after exposure to oxygen

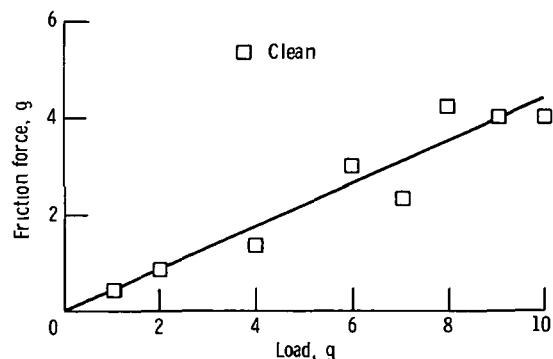
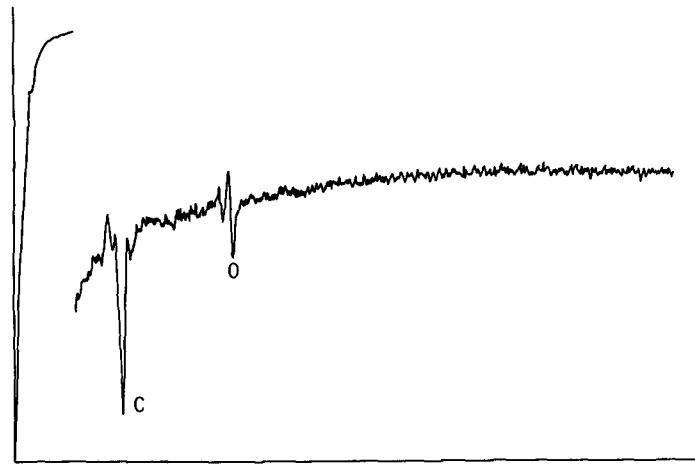
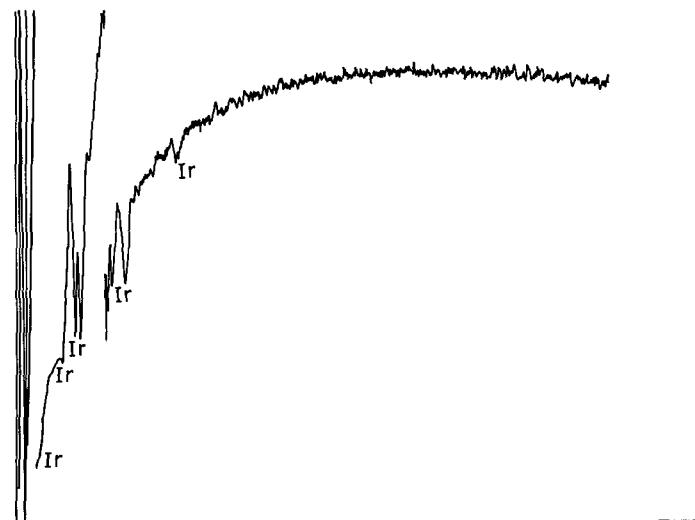


Figure 11. - Friction force as function of load for gold (111) single crystal sliding on iridium (111) single crystal.
Sliding velocity, 0.7 millimeter per minute; ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr); temperature, 23° C



(a) As obtained and placed into apparatus



(b) Sputtered clean

Figure 12 - Auger spectrum for iridium (111) surface

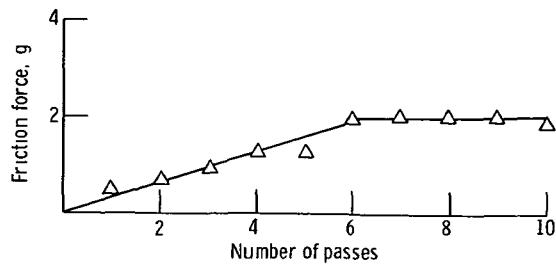


Figure 13 - Friction force as function of number of passes for gold (111) rider sliding on iridium (111) single crystal surface. Sliding velocity, 0.7 millimeter per minute, ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr), temperature, 23° C.

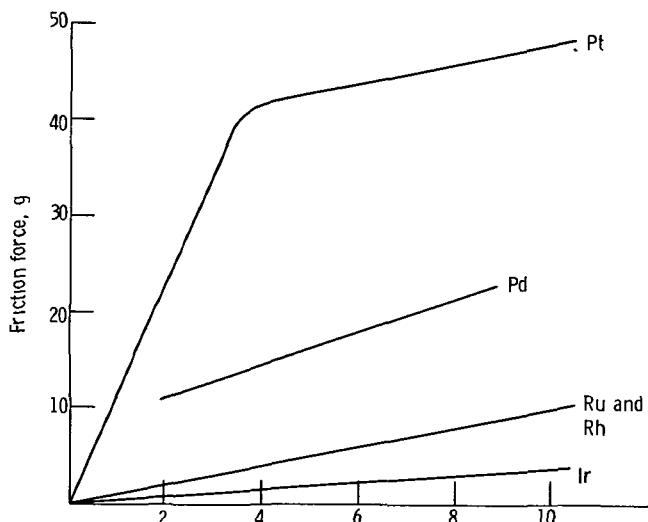


Figure 14 - Friction force as function of applied load for gold (111) single crystal sliding on various members of platinum metals group. Sliding velocity, 0.7 millimeter per minute, ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr), temperature, 23° C.

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